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(54) **MOLECULAR DECOMPOSITION PROCESS
FOR THE SYNTHESIS OF NANOSIZE
CERAMIC AND METALLIC POWDERS**

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1998.

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C01F 7/00; C01G 23/00; C01G 37/00

(52) **U.S. Cl.** **423/592.1**; 423/263; 423/607;
423/608; 423/610; 423/625; 423/594.17;
423/593.1; 423/600; 423/595; 423/596;
423/594.12; 423/598; 423/594.8

(58) **Field of Search** 423/592.1, 263,
423/607, 608, 610, 625, 594.17, 593.1,
600, 595, 596, 594.12, 598, 594.8

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LLP

(57) **ABSTRACT**

A process is disclosed for forming a nanosize ceramic powder. A precursor ceramic material is formed of a fugitive constituent and a non-soluble constituent in a single phase. The precursor is contacted with a selective solvent (water, acid, etc.) to form a solution of the fugitive constituent in the solvent and a residue of the non-soluble constituent. The precursor is sufficiently reactive with the solvent to form the solution of the fugitive constituent in the solvent and form the nondissolved residue of the non-soluble constituent. The precursor material and the non-soluble residue are sufficiently insoluble in the solvent such that there is insufficient precursor material and non-soluble residue in solution to deposit and precipitate upon the residue of the non-soluble-constituent. The fugitive constituent is sufficiently soluble in the solvent such that the precursor reacts with the solvent to form the solution of the fugitive constituent without precipitation and deposition of fugitive constituent upon the residue of the non-soluble constituent in the form of nanosize particles. After the fugitive constituent is dissolved the selective solvent containing the fugitive constituent is removed from the residue. The residue remains in the form of a nanosize powder of the non-soluble constituent.

20 Claims, 13 Drawing Sheets

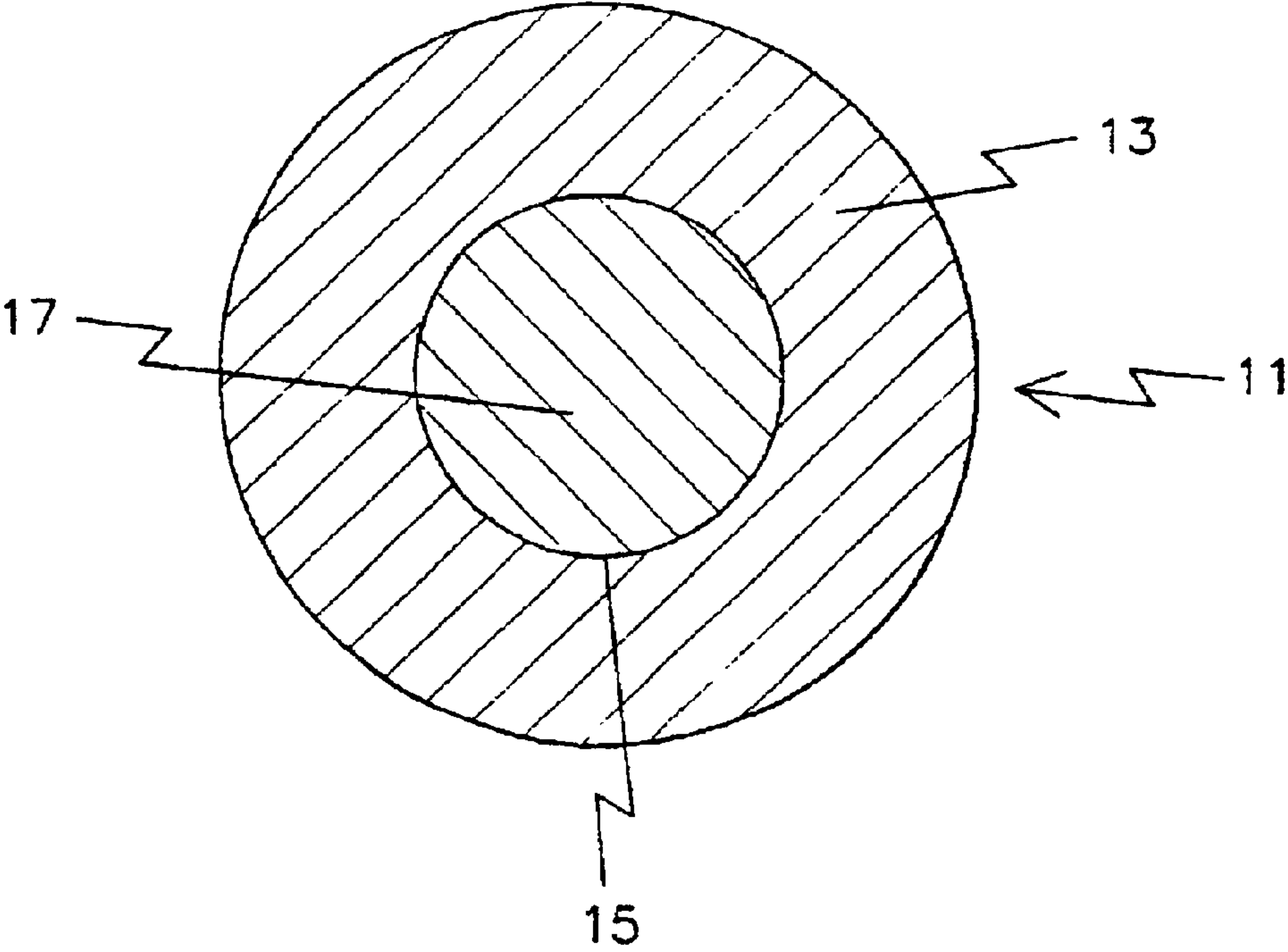


FIG. 1

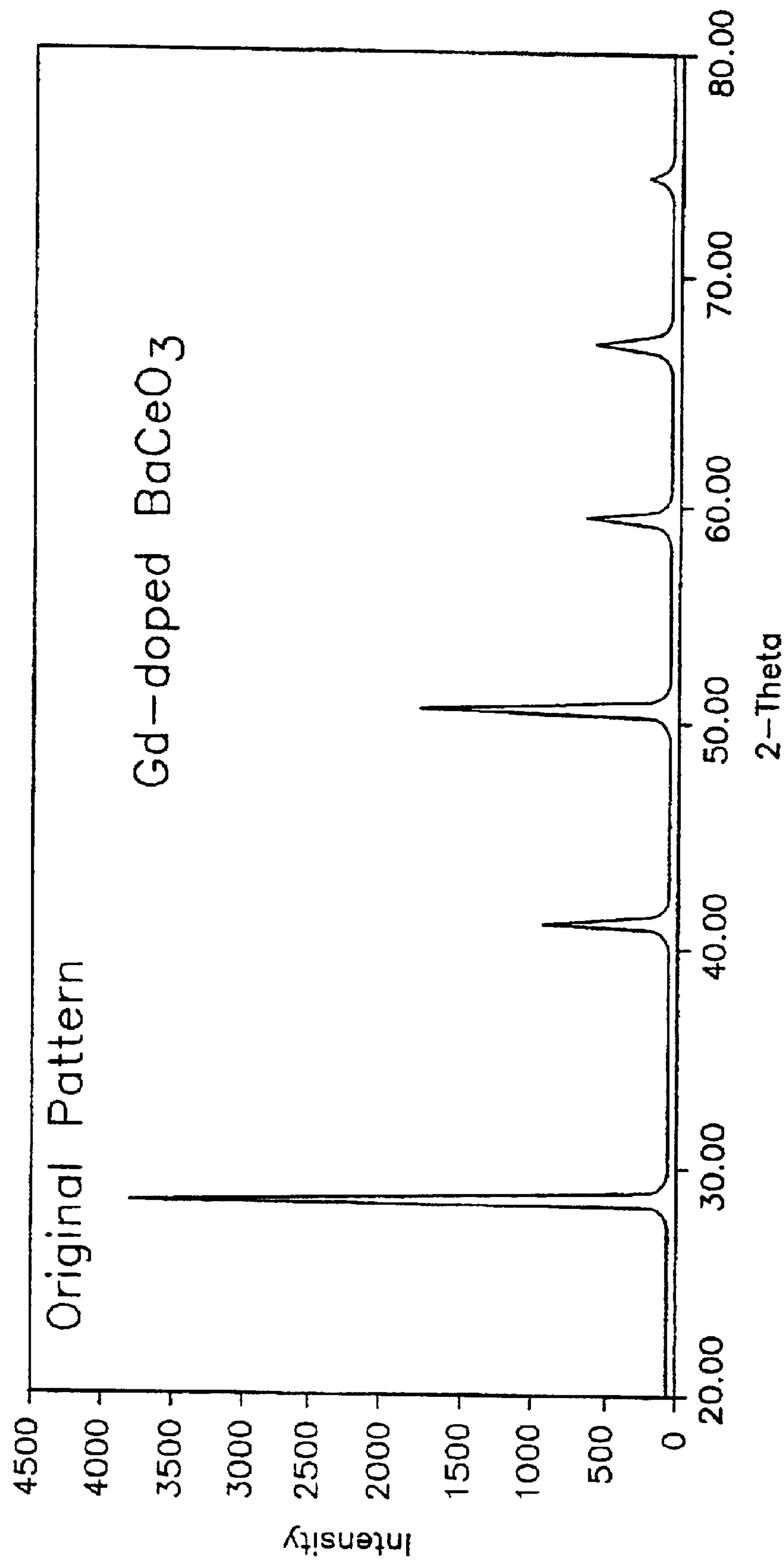


FIG. 2 (a)

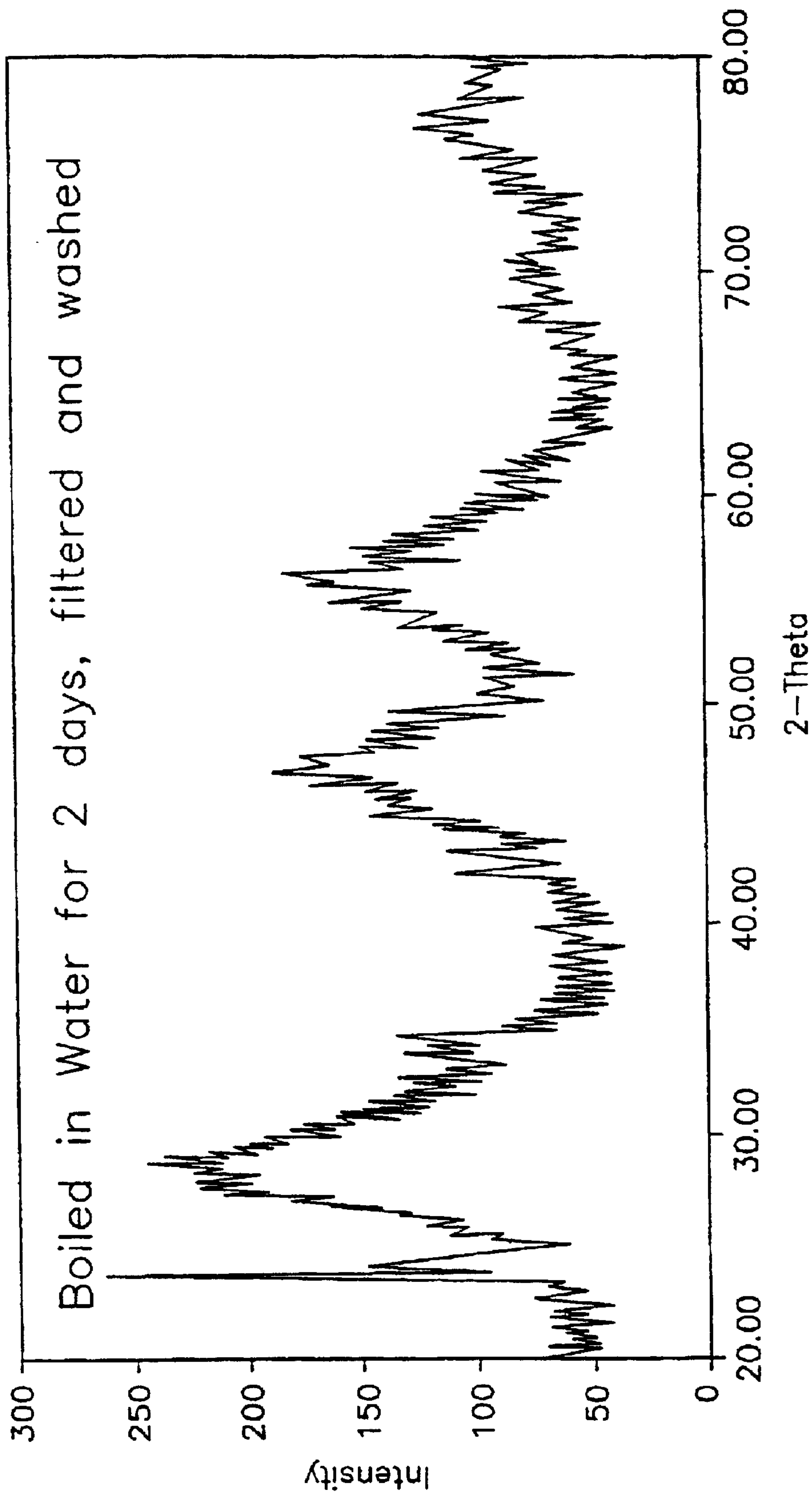


FIG. 2 (b)

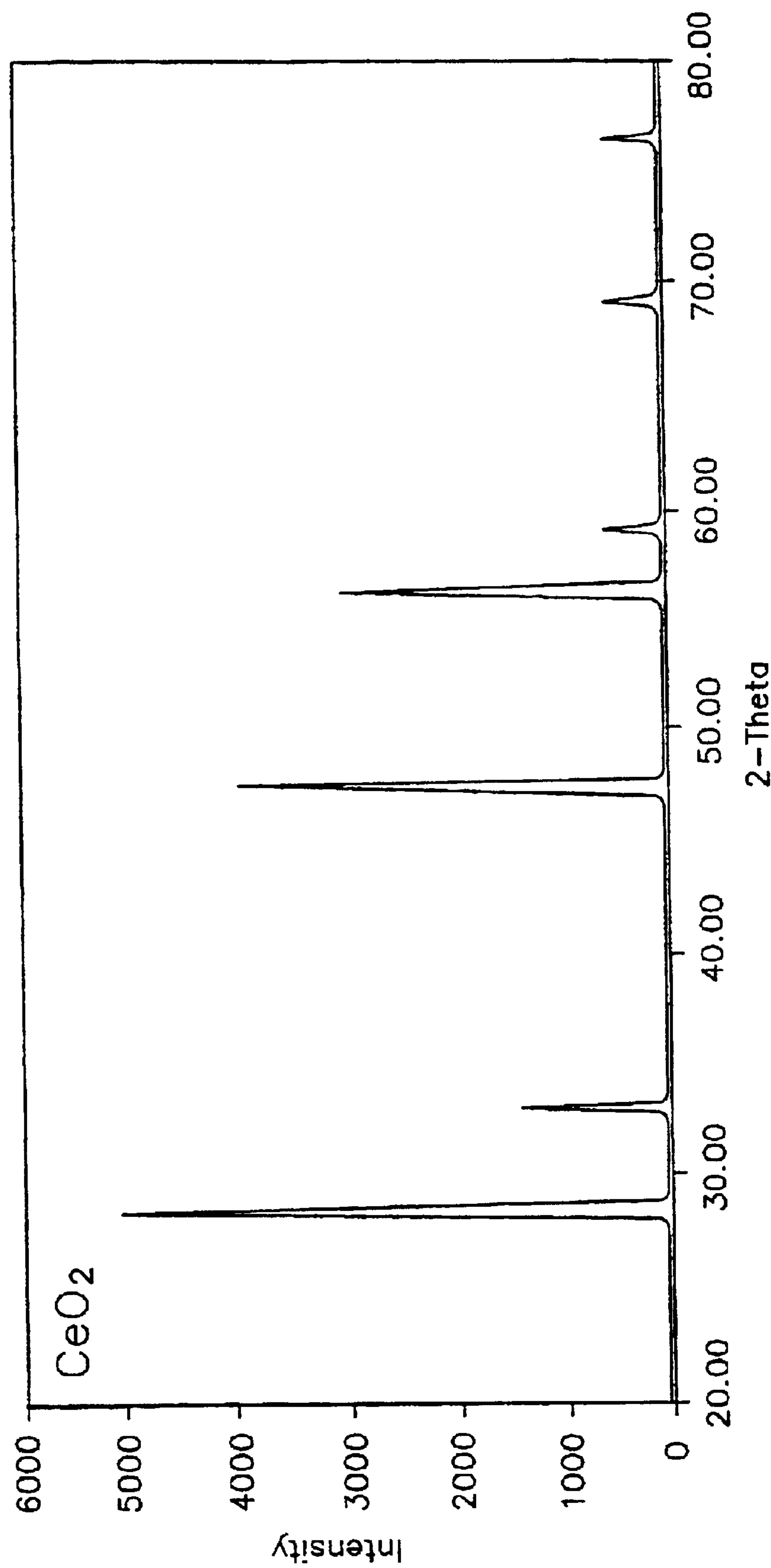


FIG. 2 (c)

Na_2ZrO_3

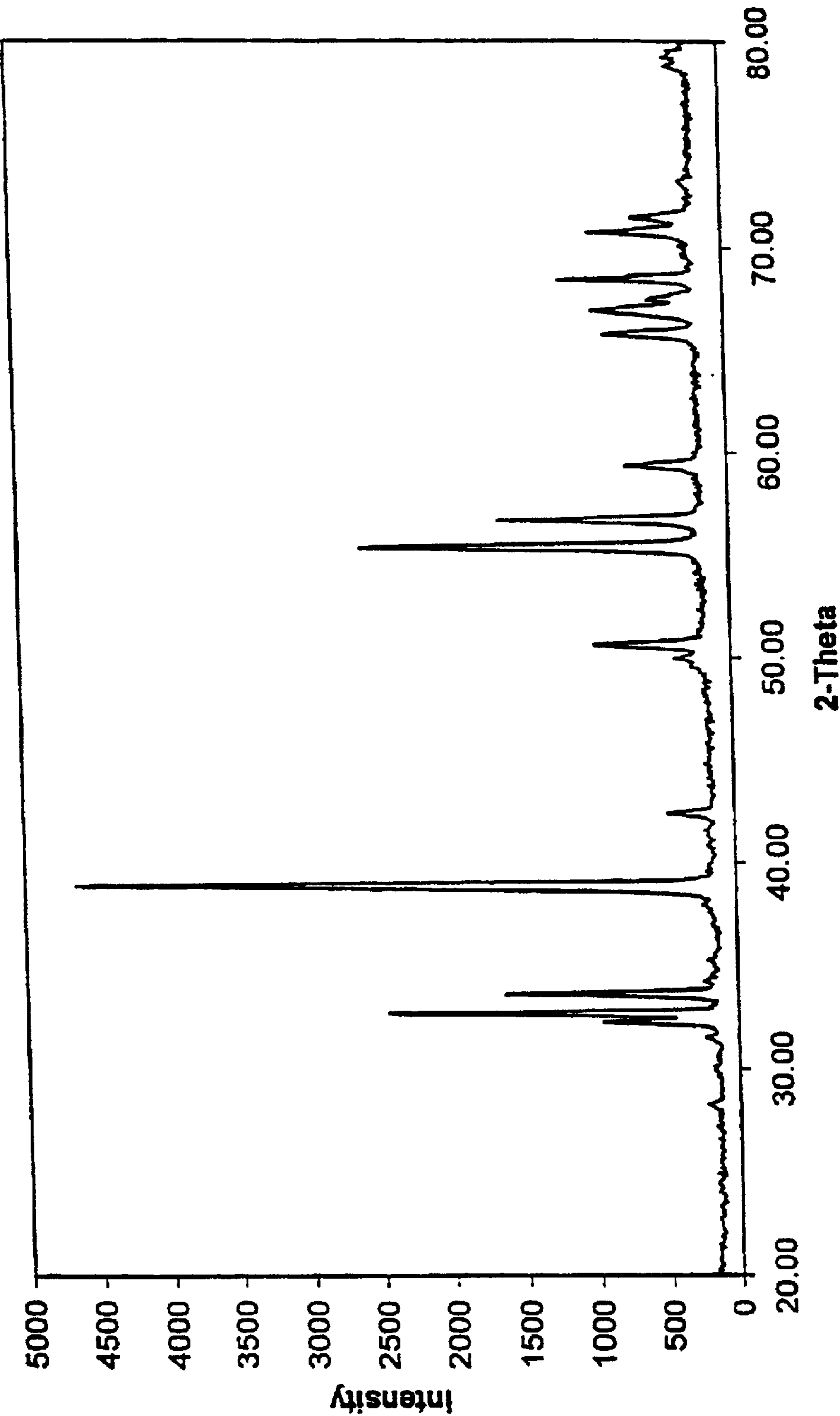


FIG. 3(a)

Na₂ZrO₃ boiled in water for 10 min

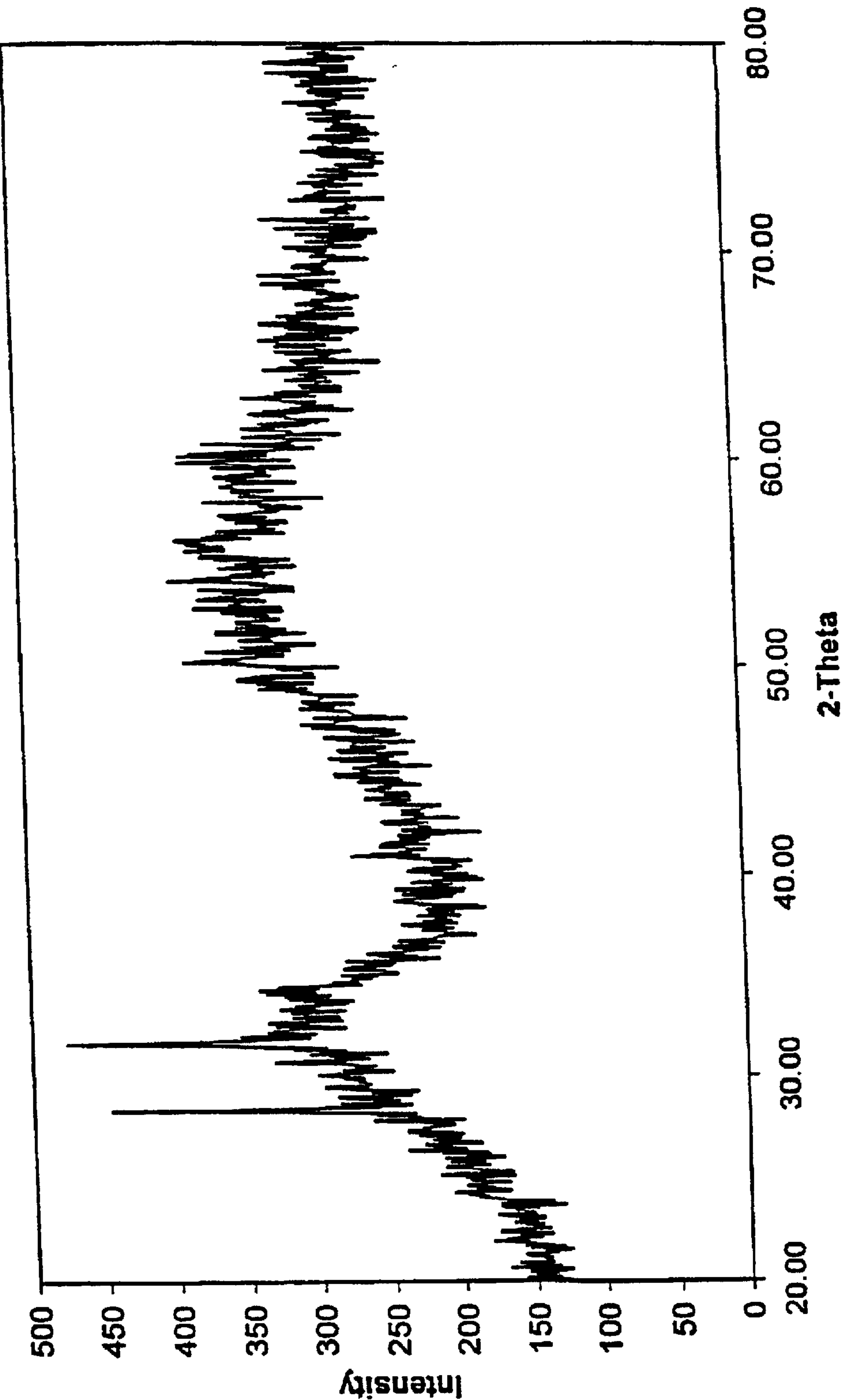


FIG. 3 (b)

Na₂ZrO₃ boiled in water for 10 min then at 100C, 1.5 hrs

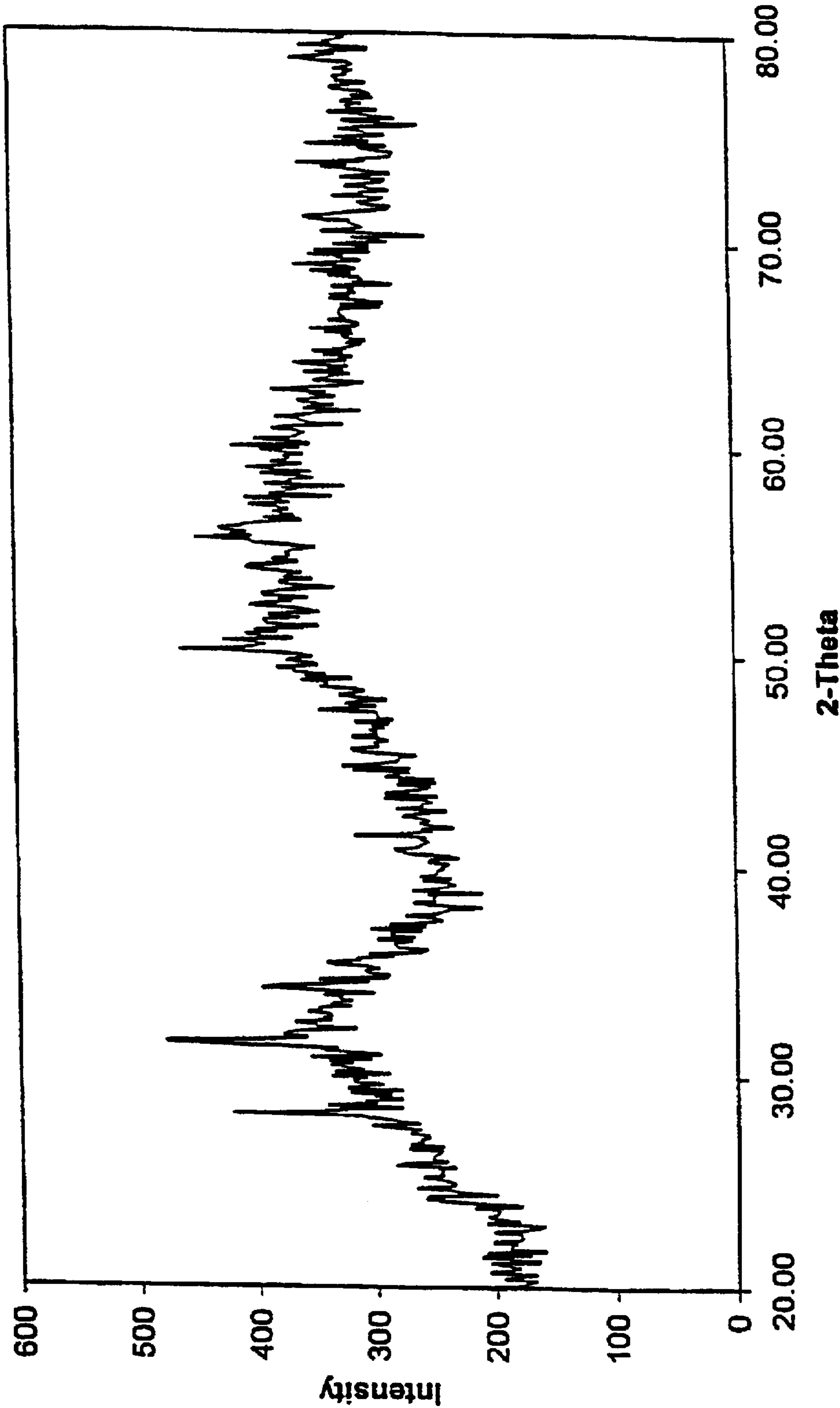


FIG. 3 (c)

Na₂ZrO₃ boiled in water for 10 min then at 200C, 1.5 hrs

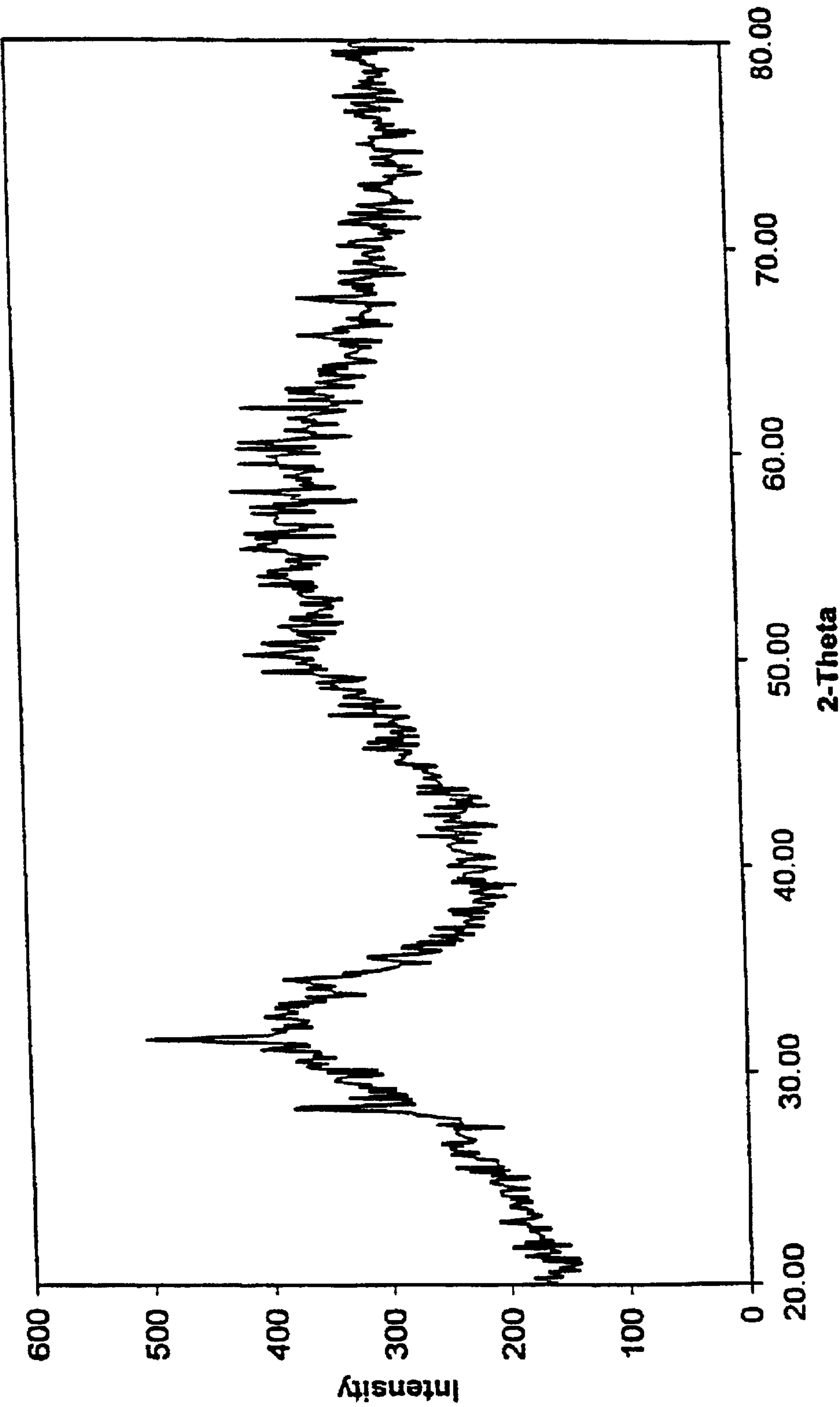


FIG. 3 (d)

Na₂ZrO₃ boiled in water for 10 min then at 300C, 1.5 hrs

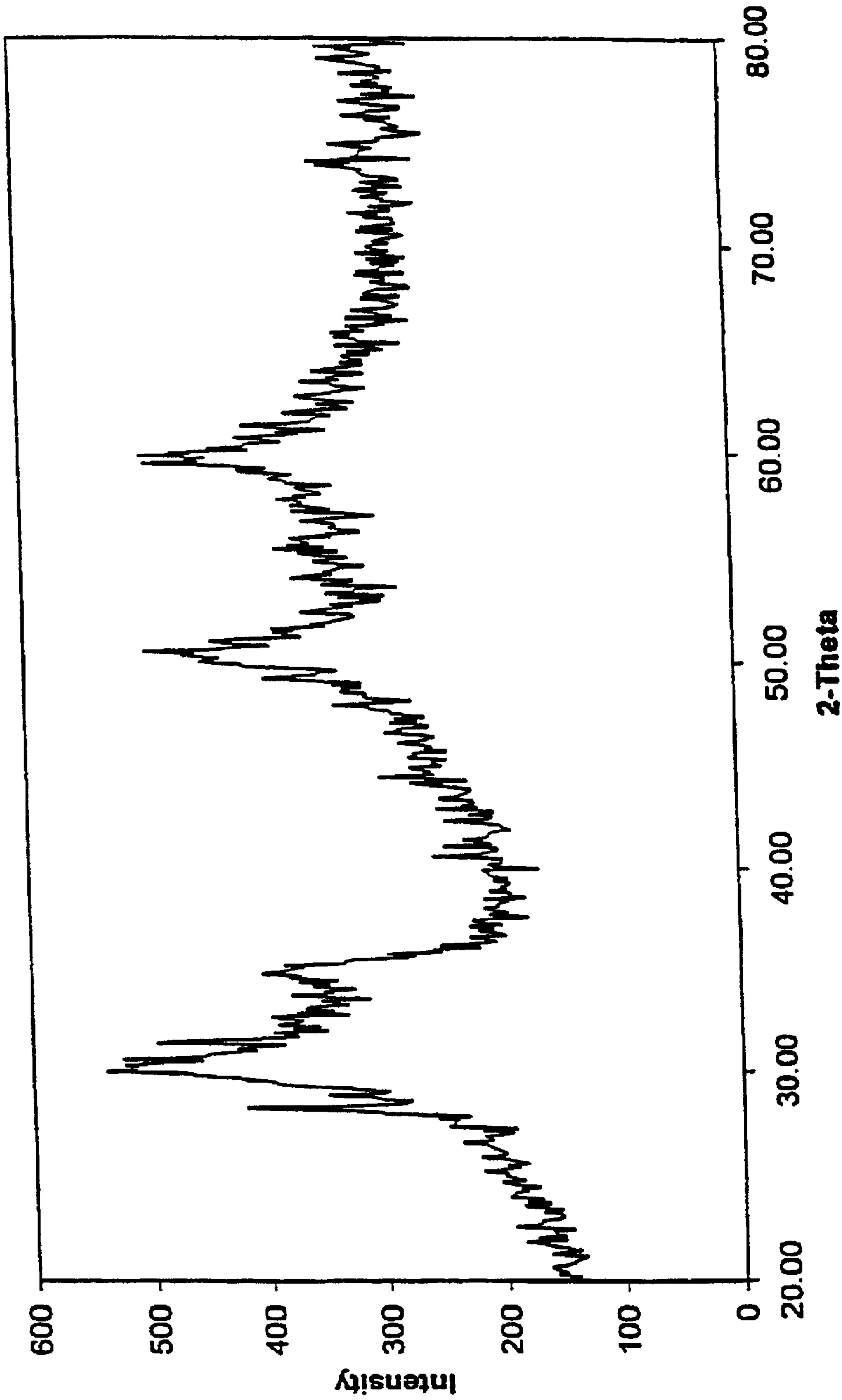


FIG. 3(e)

Na₂ZrO₃ boiled in water for 10 min then at 350C, 1.5 hrs

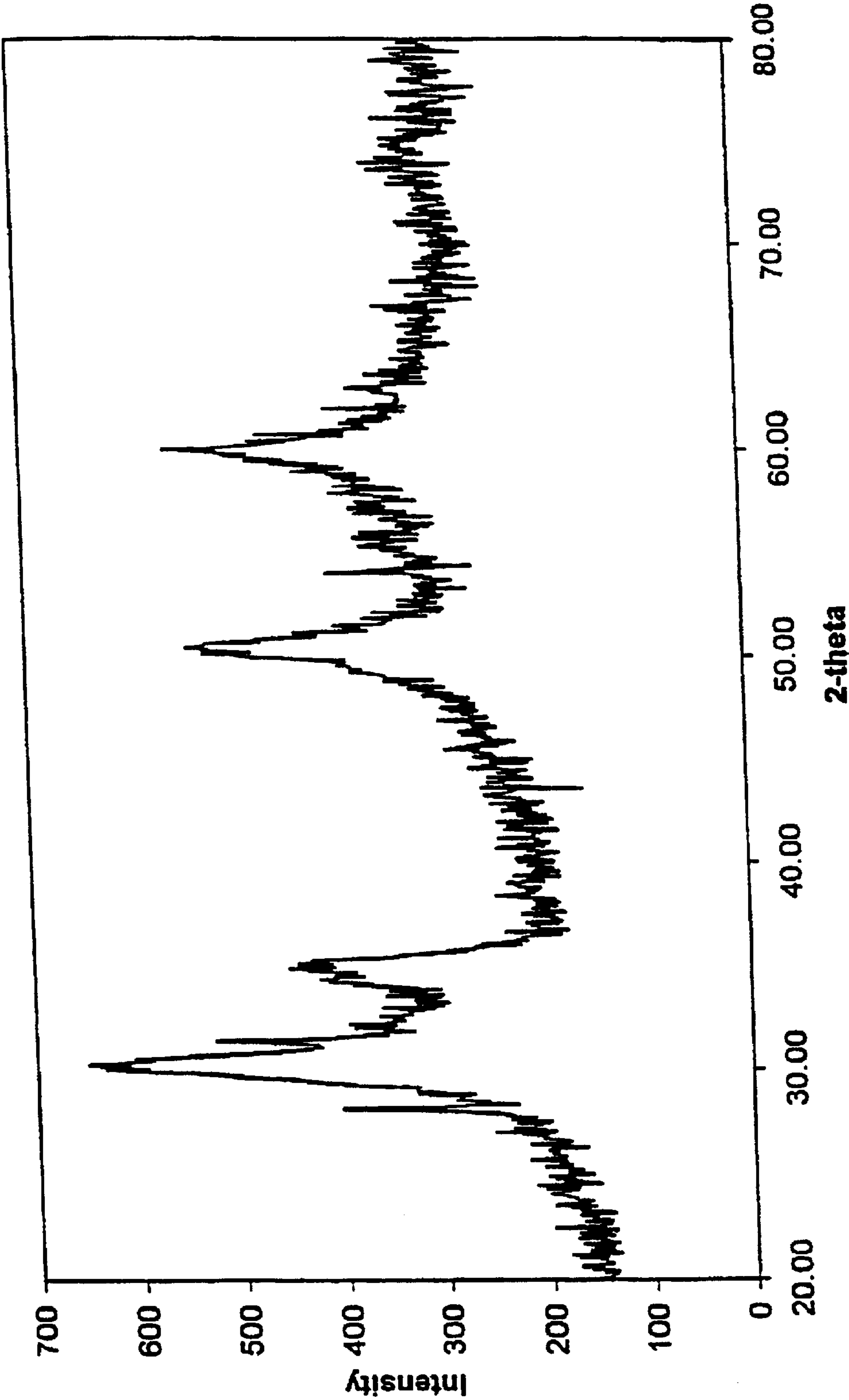


FIG. 3(f)

Na₂ZrO₃ boiled in water for 10 min then at 400C, 1.5 hrs

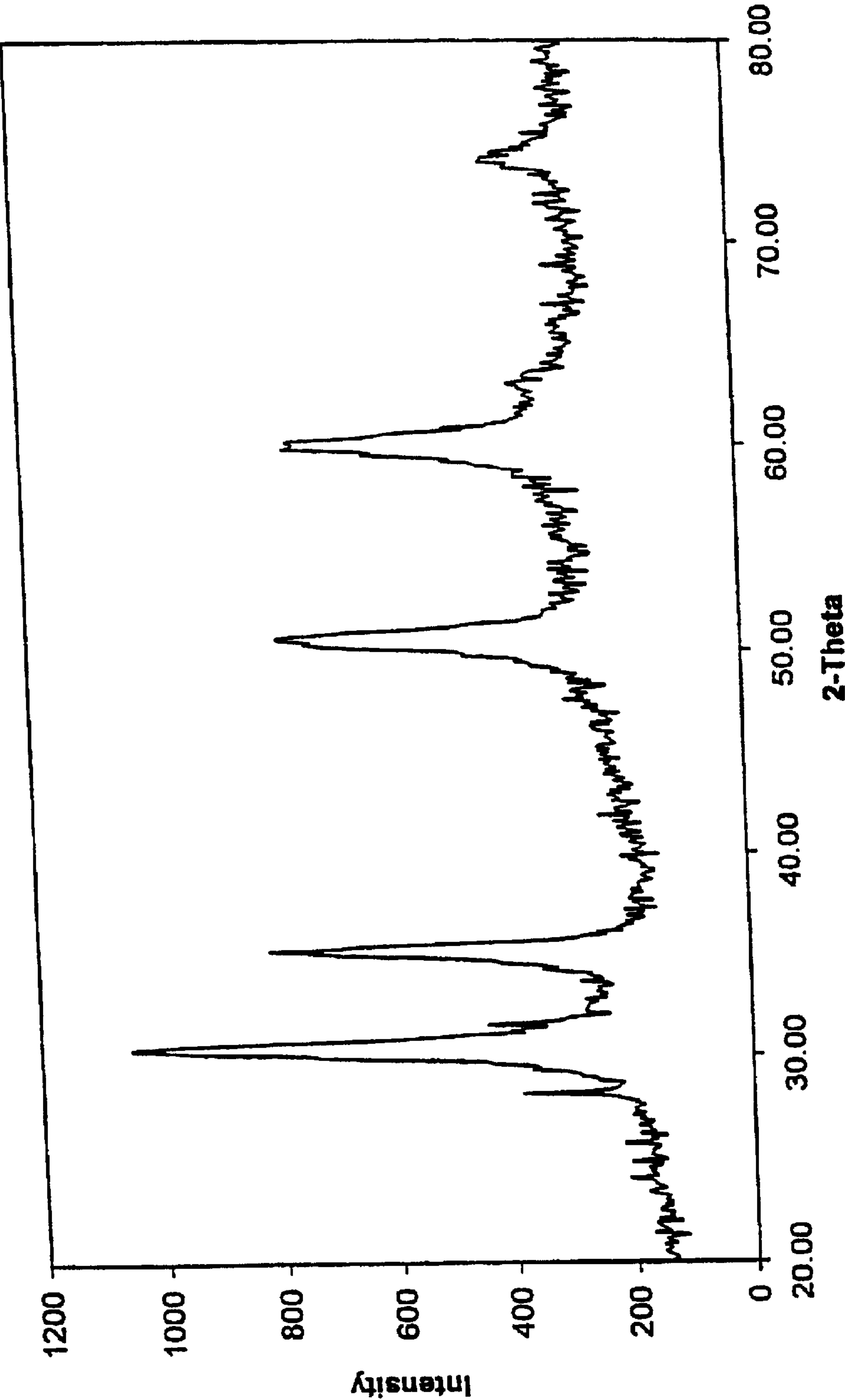


FIG. 3(g)

Na₂ZrO₃ boiled in water for 10 min then at 500C, 1.5 hrs

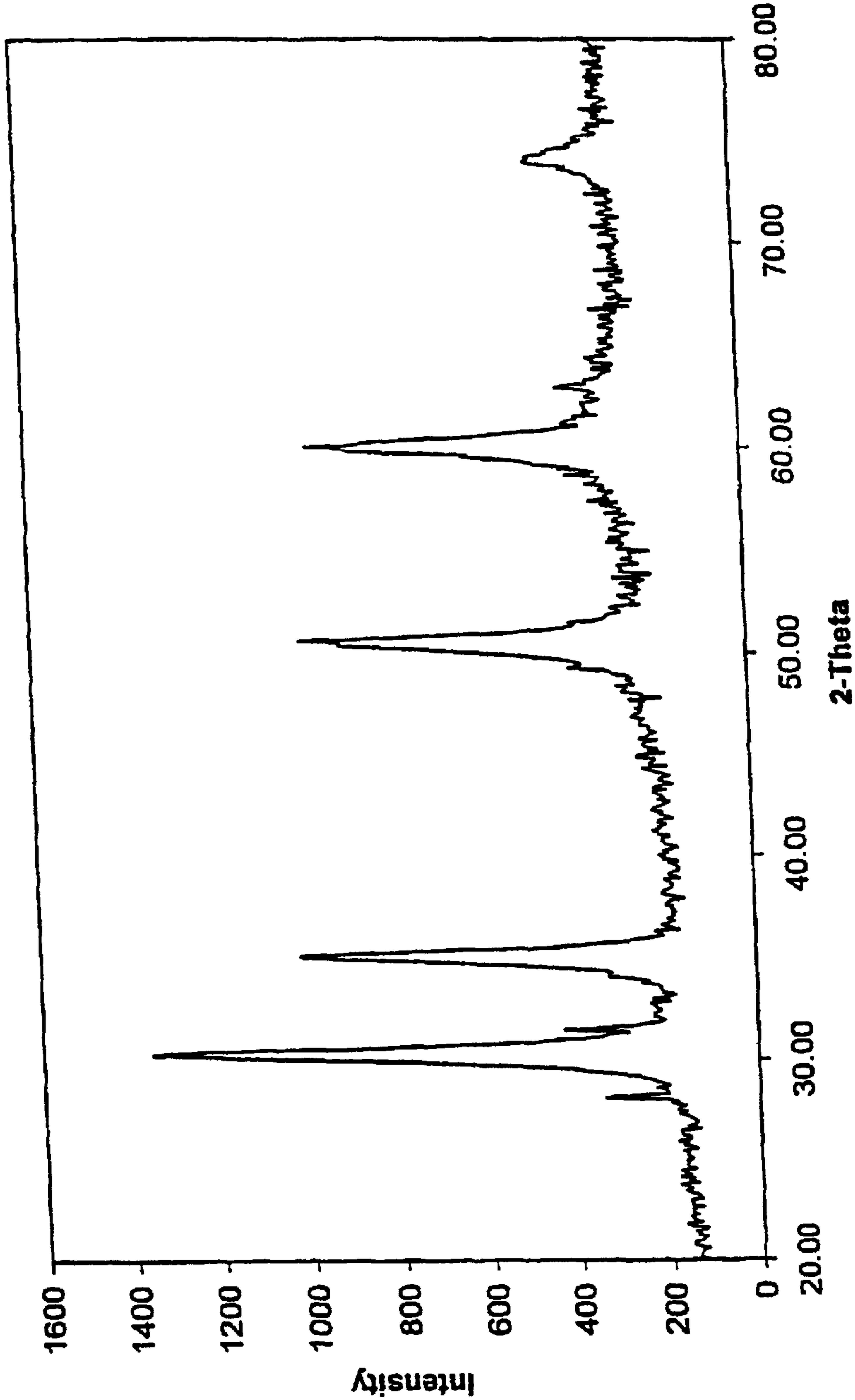
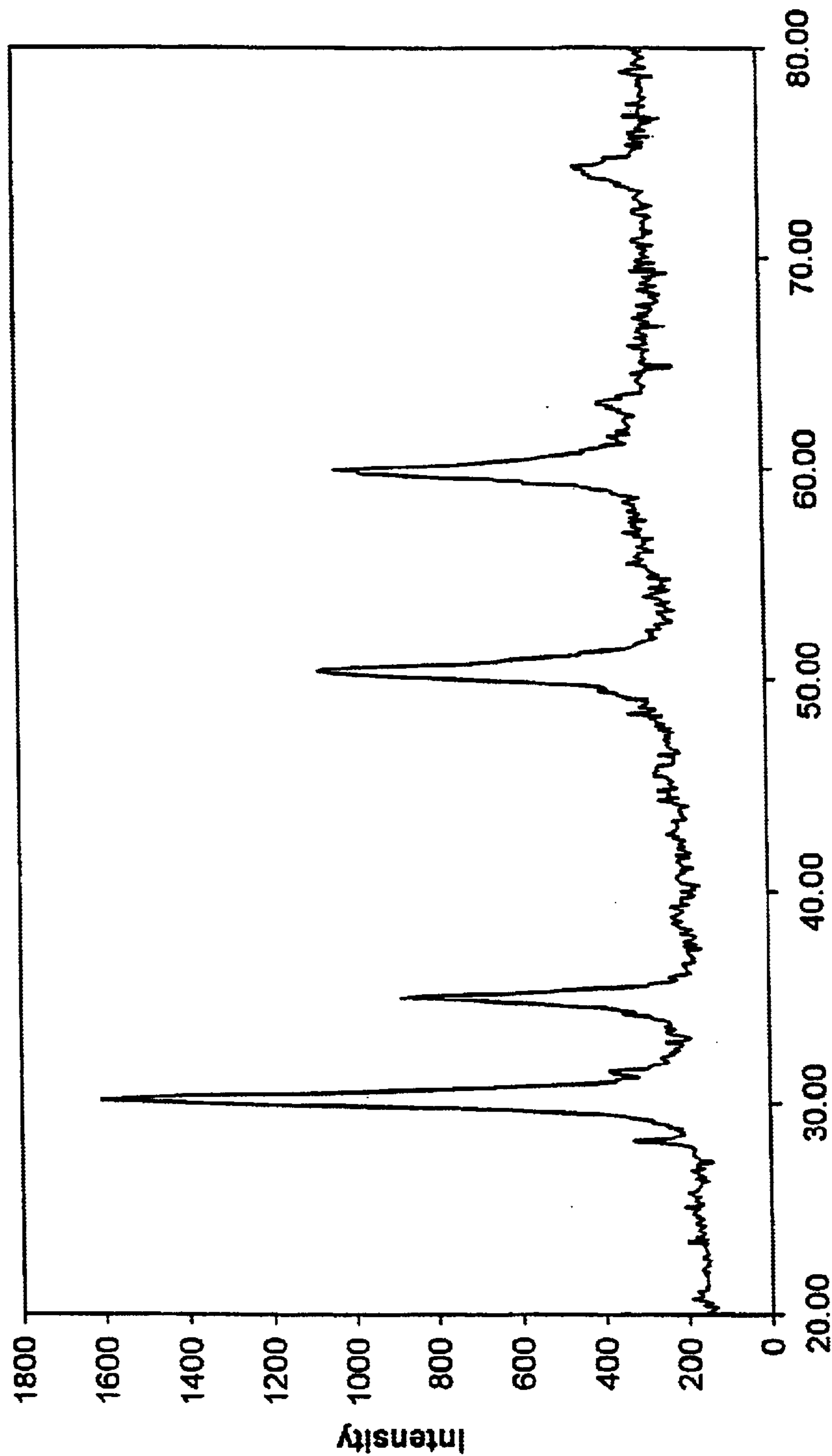


FIG. 3(h)

Na₂ZrO₃ boiled in water for 10 min then at 600C, 1.5 hrs



2-Theta

Figure 3(i)

MOLECULAR DECOMPOSITION PROCESS FOR THE SYNTHESIS OF NANOSIZE CERAMIC AND METALLIC POWDERS

This application claims benefit of provisional application 5
60/105,697 filed Oct. 26, 1998.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was developed in part with funding under 10
United States Government DOE Grant DEFG039ER45661.
The United States Government may have some rights to this
invention.

FIELD OF THE INVENTION

This invention relates to a process for forming ceramic
powders with fine nanosize particles.

BACKGROUND OF THE INVENTION

Nanosize powders are generally considered to be powders
having very fine particles in the nanometer range, i.e., less
than a few nanometers, e.g., 100 nanometers or less, usually
10 nanometers or less.

Nanosize powders have numerous applications such as 25
catalysts, electrocatalysts, catalyst supports, electrodes,
active powders for the fabrication of dense bodies, semi-
conductors for energy storage, photovoltaics, ultrafine mag-
netic materials for information storage, environmental
clean-up as destructive adsorbents, water purification, infor-
mation storage, and optical computers, to name a few. Some
of the numerous examples include the following:
nanosize (3 to 4 nm) platinum for oxygen reduction in acid
electrolytes, many metallic powders made by precipitation
in aqueous and non-aqueous media for alloy fabrication and
for catalysis, nanosize iron oxide catalyst for coal
liquefaction, nanosize iron oxide particles for magnetic
applications, tetragonal zirconia powder by a hydrothermal
treatment at high pressures for structural applications, car-
bides and nitrides using non-aqueous media, nanosize 40
 BaTiO_3 by a gas-condensation process, etc. Many oxides
have potential applications as nanosize powders. These
include: $\text{CeO}_{(2-x)}$ for catalytic reduction of SO_2 , γ -alumina as
a catalyst support and for enhancing ionic conductivity of
lithium iodide, V_2O_5 as a catalyst for NO_x reduction, and
etc. Several processes currently used for the synthesis of
nanosize powders include: (1) Gas-phase condensation, (2)
Mechanical milling, (3) Thermal crystallization, (4) Chemi-
cal precipitation, (5) Sol-gel processing, (6) Aerosol spray
pyrolysis, and etc.

In gas-phase condensation, evaporation of precursors and
their interaction with an inert gas leads to loss of kinetic
energy, and homogeneous nucleation of nanosize powders
occurs in a supersaturated vapor. Nanocrystalline powders
of TiO_2 , Li_2O -doped MgO , CeO_2 , Y-doped ZrO_2 , etc. have 55
been produced by gas-phase condensation. Aerosol spray
pyrolysis has been used to synthesize $\text{BaFe}_{12}\text{O}_{19}$, Fe_2O_3
among some other materials. High-energy mechanical mill-
ing is used extensively to produce nanostructured materials,
especially when large quantities of materials are required. 60
Very fine particles of nickel-aluminum alloy, Fe—Co—Ni—
Si alloys, Ni—Mo alloys, for example, have been produced
by mechanical milling. Contamination by the milling
process, however, is a shortcoming of this process. Also,
although very fine (nm size) particles can be made, agglom-
eration is a problem leading to cluster sizes in the micron
range.

Chemical coprecipitation has received considerable atten-
tion for the synthesis of nanosize powders. Metallic as well
as ceramic powders can be made by a careful control of
chemistry. Alkali metal borohydride, MBH_4 where M is an
alkali metal, for example, has been used as a reducing agent
in aqueous media for the synthesis of metallic powders.
Similarly, hydroorganoborates of the general formula MH_v
(BR_3) or $\text{MH}_v[\text{BR}_n(\text{OR}')_{3-n}]_v$ where M is an alkali or alka-
line earth metal, $v=1, 2$, and R, R' are alkyl or aryl groups
have been used as reducing and precipitating agents. It is
important to control pH and ionic strength in aqueous media
to prevent Ostwald ripening. In the synthesis of nanosize
iron oxide, for example, it has been shown that the higher the
pH and the higher the ionic strength, the smaller is the size
15 of nanosize Fe_3O_4 particles.

In most methods for the synthesis of nanosize powders,
two issues are particularly important; (1) the formation of
fine, uniform size particles, and (2) the prevention of
agglomeration. Nanoparticles of a uniform size can in prin-
ciple be formed by carefully controlling nucleation and
growth. Often, a variety of encapsulating methods are nec-
essary to control the size of nanoparticles.

Agglomeration is often the result of Van der Waal's
forces. The adverse effect of agglomeration on the sintering
behavior of ceramic powders is well documented. Even in
catalysis, the need for dispersed powders is well known.
Often, supercritical drying can be used to obtain nonag-
glomerated powders. In liquid media, agglomeration can be
suppressed through steric hindrance or through the manipu-
lation of electrostatic interactions. The latter in polar liquids
can be achieved by changing the pH and the ionic strength
of the solution. Many techniques involve the use of surfac-
tants. Often the powders which are nonagglomerated and
well dispersed in a liquid, tend to agglomerate during the
drying stage. Fortunately, methods such as slip-casting,
gel-casting, pressure slip casting can be used to achieve
powder compaction in a wet state. Such has been demon-
strated using submicron ceramic powders.

With the exception of milling, all the above methods are
based on molecular synthesis of nanoparticles wherein the
particles are built-up by atom-by-atom, or molecule-by-
molecule, addition. Even in processes based on the decom-
position of metal carbonyls, the growth of particles occurs
by a layer-by-layer addition of atoms. As a result, a control
of nucleation and growth is necessary to ensure the forma-
tion of nanosize particles. This often requires a very precise
and difficult control of the reaction system, which renders
the manufacture of the nanosize powder in large quantities
impractical or impossible. In addition, the molecular syn-
thesis processes are costly because of the relatively large
capital expenditures required for the equipment to control
the formation of only a small quantity of nanosize product.

OBJECTS OF THE INVENTION

It is, therefore, an object of the invention to provide
method for the formation of nanosize powders that is easy to
implement on an industrial scale and in relatively inexpen-
sive when compared to molecular synthesis methods.

Another object of the invention is to provide a method in
which nanosize powders are formed by a process other than
precipitation or deposition from solutions, thus eliminating
the possibility of unwanted deposition and growth of the
nanosize powders.

Another object of the invention is to provide a method 65
which forms nanosize powders that have a reduced tendency
to agglomerate.

Another object of the invention is to provide a method for the formation of nanosize powders that can be applied to forming a variety of powder compositions.

Further objects of the invention will become evident in the description below.

BRIEF SUMMARY OF THE INVENTION

In order to overcome the problems associated with molecular synthesis and milling to form nanosize powders, the present invention presents an alternative approach for the synthesis of nanosize powders. In the present invention, a precursor inorganic compound is formed from which the unwanted component is leached away so that a fine, nano-size powder is left as a residue. Thus, the present invention is based on molecular decomposition, rather than molecular synthesis, or deposition.

As discussed above, one of the problems with many methods of synthesis of nanosize powders is that often it is difficult to synthesize large quantities of materials. By contrast, the present invention is suitable for making large quantities of nanosize powders of a number of materials.

In summary, the present invention is a process for forming nanosize powders. The process comprises:

forming a precursor ceramic material comprising a fugitive constituent and a non-soluble constituent in a single phase;

contacting the precursor material a selective solvent to form a solution of the fugitive constituent and a residue of the non-soluble constituent, the precursor sufficiently reactive with the solvent to form the solution of the fugitive constituent in the solvent and the residue of the non-soluble constituent the precursor material and the non-soluble residue sufficiently insoluble in the solvent such that there is insufficient precursor material and non-soluble residue in solution to deposit and precipitate upon the residue of the non-soluble-constituent, the fugitive constituent being sufficiently soluble in the solvent such that the precursor reacts with the solvent to form a solution of the fugitive constituent without precipitation and deposition of fugitive constituent upon the residue of the non-soluble constituent in the form of nanosize particles;

removing the selective solvent solution from the residue to form a nanosize powder having the same chemical composition as the non-soluble constituent.

The precursor material should be insoluble as the precursor material in the solvent. One of the objects of the present invention is to prevent deposition or precipitation of dissolved materials upon the nanosize particles that are formed from the non-soluble residue freed of the fugitive constituent. Deposition or dissolved precursor material will not only contaminate the residue, but possibly result in particles that are too large. In the present invention, an object is to prevent, as much as possible, deposition of dissolved materials and the resulting growth of existing crystals. Unlike prior-art methods where small crystals are crystallized from solution, it is practical in the present invention to inhibit the crystallization and precipitation process altogether, as crystallization is not required to form initial nanosize crystals. Accordingly, as further illustrated below, a precursor is chosen such that precipitation of any material upon the nanosize particles is essentially avoided.

Another requirement of the precursor material is that it be reactive with the solvent. Since the precursor is insoluble, the precursor composition does not dissolve, but it does react to selectively remove the fugitive constituent, leaving a

freed non-soluble constituent. The fugitive constituent is sufficiently soluble that it will not precipitate from the solution to contaminate and grow the particles of the non-soluble constituent. The non-soluble constituent is essentially insoluble to prevent dissolved material dissolving into the solution, there thereafter precipitating upon and growing the nanosize particles of the non-soluble material formed by removal of the fugitive constituent. Basically, the invention involves a balance between preventing precursor and non-soluble constituent from forming a solution so that it cannot redeposit and grow crystals, and removing the fugitive constituent, that is sufficiently soluble in the solution that it will not precipitate from the solution to grow crystals.

For example, BaCeO_3 does not dissolve in water, but reacts with water to form a solution of the Ba (as $\text{Ba}(\text{OH})_2$). On the contrary, NaAlO_2 is soluble in water, and cannot be used as a suitable precursor for the present invention.

In order that the non-soluble constituent freed from the fugitive constituent form nanosize particles, the precursor should be a single phase material, i.e., where the differentiation between the non-soluble and the fugitive constituents is on a molecular level. Accordingly, the precursor exists as a compound existing in the form of a large molecule, or as an alloy. For ceramics, an example of a precursor material is a mixed oxide with at least two cations, the metal oxide of the first cation being soluble to function as the fugitive constituent, and the oxide of the second being non-soluble to function as the non-soluble constituent. For forming, metal nanosize powders, the precursor can exist, for example, as an alloy or an intermetallic compound.

The solvent is selected to react with the precursor and have the solubility properties as described above. For ceramics, a preferred solvent is water, but non-aqueous solvents may be required to suppress the solubilities of the non-soluble residue and/or the precursor. Usually the solvent is polar, as the fugitive constituent, which must be solubilized, is often a polar composition. Typically, suitable solvents for forming a ceramic nanosize powder are polar liquids that solubilize selected ceramic oxides, which selected oxides in the process of the invention are the fugitive constituents. As further described below, preferred solvents are water and acids. For metallic nanosize powders, the selective solvent is typically an acid that reacts with or dissolves the fugitive metal, and not the non-soluble metal. In place of acids, an acid gas such as SO_3 , N_2O_5 , CO_2 or HCl , may be used to react with and remove the fugitive constituent.

Any suitable process may be used for forming a precursor is contemplated.

For example, where the precursor is a mixed ceramic subjecting a powder mixture to a suitable high-temperature treatment is suitable. Precursors for metallic powders are likewise formed by any suitable process to produce a suitable alloy or intermetallic compound, such as alloying methods or powder metallurgy.

The solvent is then removed from the remaining non-soluble constituent. With the fugitive constituent removed, the non-soluble constituent assumes the form of nanosize particles. The solvent is removed by conventional methods, including, but not limited to settling, centrifugation, filtering, air drying, or a combination of the above. The solvent, may also be removed by replacing it with another liquid, such as replacing an aqueous solvent with an alcohol, and then separating the powder from the replacement liquid. Using a replacement liquid may be desirable to inhibit agglomeration of the powder during drying.

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The product is chemically the same as the non-soluble constituent. The process of the invention is particularly suitable for synthesizing nanosize powders of Al_2O_3 , CeO_2 , ZrO_2 , TiO_2 , V_2O_5 , rare earth (RE) oxide-doped CeO_2 and RE- or Y_2O_3 -doped ZrO_2 .

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing a reaction illustrative of the process of the invention

FIG. 2(a) is an XRD (X-ray diffraction) trace of a single-phase perovskite precursor material (Gd-doped BaCeO_3).

FIG. 2(b) is an XRD trace of the material of FIG. 2(a) after boiling in water for two days, showing conversion to nanosize CeO_2 .

FIG. 2(c) is an XRD trace of a comparative coarse (not nanosize) CeO_2 powder.

FIG. 3(a) is an XRD trace of an as-received, precursor (non-nanosize) Na_2ZrO_3 powder.

FIG. 3(b) is an XRD trace of the residue after boiling the Na_2ZrO_3 of FIG. 3(a) in water for 10 minutes.

FIG. 3(c) is an XRD trace of the residue from the boiling of Na_2ZrO_3 from FIG. 3(c) after heating in air to 100°C . for 1.5 hours.

FIG. 3(d) is an XRD trace of the residue after 1.5 hours in air at 200°C .

FIG. 3(e) is an XRD trace of the residue after 1.5 hours in air at 300°C .

FIG. 3(f) is an XRD trace of the residue after 1.5 hours in air at 350°C .

FIG. 3(g) is an XRD trace of the residue after 1.5 hours in air at 400°C .

FIG. 3(h) is an XRD trace of the residue after 1.5 hours in air at 500°C .

FIG. 3(i) is an XRD trace of the residue after 1.5 hours in air at 600°C .

DETAILED DESCRIPTION OF THE INVENTION

Synthesis of Precursor Powders

The present invention is suitable for the synthesis of many types of powders. Although the following discussion is confined to specific materials, the applicability of the present invention to other powders will be evident to one of ordinary skill in the art. For the purposes of discussion, rare earth (RE)-doped CeO_2 and Y_2O_3 -doped ZrO_2 are used as examples. Y_2O_3 -doped ZrO_2 has many applications such as in oxygen sensors, solid oxide fuel cells, as a constituent in electrodes and in structural ceramics. RE-doped CeO_2 has applications in oxygen separation membranes, in fuel cells as well as in catalysis.

Respective precursor powders can be synthesized using conventional processing methods. For example, for the synthesis of nanosize RE_2O_3 -doped CeO_2 by the present invention, a precursor can be $\text{BaCe}_{(1-x)}\text{RE}_x\text{O}_{(3-\delta)}$. The precursor is synthesized using BaCO_3 , RE_2O_3 and CeO_2 in a powder form, mixing reagent powders, and calcining at 1250°C . A similar procedure can be used for other materials such as Y_2O_3 -doped ZrO_2 . Other examples included $\text{BaCe}_{(1-x)}\text{RE}_x\text{O}_{3-\delta}$ or $\text{SrCe}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ precursors for a composition of the final nanosize powder is $\text{Ce}_{1-x}\text{RE}_x\text{O}_{2-\delta}$, or $\text{BaZr}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ or $\text{BaZr}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ precursors for a composition of the nanosize powder of $\text{Zr}_{1-x}\text{RE}_x\text{O}_{2-\delta}$ RE is a rare earth metal or Y, x is between 0 and about 0.25, and δ is between 0 and about 0.13.

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Synthesis of Nanosize Powders from the Precursor

Synthesis of the nanosize powders from the precursor involves exposing the precursor to a selective solvent that leaves the desired component. The following approaches can be used:

(a) A reaction with water.

(b) A reaction with a dilute acid such as HNO_3 , HCl , H_2CO_3 , and H_2SO_4 .

(c) A reaction with CO_2 and SO_3 in polar, non-aqueous solvents.

(a) A Reaction with Water

Water is the ideal solvent. Also, in many cases, thermodynamics of the formation of alkali hydroxides or alkaline earth hydroxides are favorable. There are, however, a few potential complications, in particular many elements form hydroxides, and there is the danger of agglomeration during the drying stage. For example, in the synthesis of ZrO_2 the undesired formation of $\text{Zr}(\text{OH})_4$ is possible. However, it has been shown that with Na_2ZrO_3 as a precursor, a direct reaction with water can be readily effected without the formation of $\text{Zr}(\text{OH})_4$. The potential for agglomeration can be suppressed by replacing the water with alcohol after solvation.

(b) A Reaction with Acids

In many cases, reaction with water is not favorable. For example, reaction of BaZrO_3 with water to form ZrO_2 and $\text{Ba}(\text{OH})_2$ is not favored. However, as shown in Table B, reaction of BaZrO_3 with HNO_3 or N_2O_5 to form $\text{Ba}(\text{NO}_3)_2$ and ZrO_2 is favored. Also, $\text{Ba}(\text{NO}_3)_2$ has a reasonable solubility in water. With HNO_3 as a reactant, the formation of $\text{Zr}(\text{OH})_4$ is suppressed. The tendency for agglomeration can be minimized, by either replacing water with an alcohol or other organic liquids of high vapor pressures, or drying under supercritical conditions. It is also within contemplation of the invention to use surfactants to minimize agglomeration, either based on electrostatic interactions or steric effects.

(c) Reactions with Non-aqueous Electrolytes—Reactive Gases in Polar, Non-aqueous Solvents

This approach is particularly suitable when there is a tendency to form hydroxides of the product oxides which precludes the use of water when the objective is to synthesize nanosize powders with minimal agglomeration. In such cases, the use of non-aqueous, polar liquids may be necessary. Table C lists a few non-aqueous solvents, which are used for non-aqueous electrolytes. The polar liquid used as a solvent should also have a reasonable solubility for the reacting gas, which may be, for example, CO_2 , SO_3 , SO_2 , or N_2O_5 .

Suitable solvents are selected based on the following criteria: (i) the solubility of the reacting gas in the solvent, and (ii) the solubility of the fugitive compound formed; e.g. BaCO_3 or BaSO_4 in the case of CO_2 or SO_3 . In order to increase contact between the precursor powder (e.g. $\text{BaGd}_x\text{Ce}_{(1-x)}\text{O}_{(3-\delta)}$, $x=0-0.25$, $\delta=0-0.13$) and the gas (CO_2 or SO_3), the suspension of the powder is preferably agitated, e.g. by constant stirring, while the gas is bubbled through it. The solvent vapors are also preferably recovered and returned back to the reactor, by using, for example, a water-cooled condenser.

Mechanism of the Kinetics of Synthesis of Nanosize Powders

The kinetics of the formation of nanosize powders is a factor that should be considered in choosing the precursor and solvent for the desired. The data in Table B give the thermodynamic basis for the occurrence of certain given reactions. Assuming a given reaction is favored over undes-

ired competing reactions, an important consideration is the kinetics of the reaction. With reference to the schematic of the reaction given in FIG. 1, it is readily seen that the kinetics of the reaction should depend upon the transport of soluble reactants and products. The overall reaction mechanism is expected to involve the following steps; (a) The transport of the dissolved reacting gas, e.g., N_2O_5 , CO_2 or SO_3 , (or the respective acids) through the porous layer formed to the interface separating the precursor and the product, (b) Reaction at the interface, and (c) The transport of the dissolved byproduct, e.g., $Ba(NO_3)_2$, $BaCO_3$ or $BaSO_4$, from the interface through the porous layer, into the bath. The overall kinetics may be influenced by all three of the factors, and may be dictated by whichever is the slowest step. The solubility of the reacting gas is a function of pressure; the higher the pressure, the higher is the solubility. Both the kinetics of the actual reaction occurring at the interface as well as the transport through the porous layer are functions of the concentration of the dissolved reactant species; the higher the concentration, the faster should be the kinetics. The temperature dependence of the reaction at the interface, however, will in general be different from that of the transport of dissolved species. The known theoretical models of transport through porous bodies can be used in this analysis.

Propensity for Particle Growth

The advantage of the present invention over the other methods for the synthesis of nanosize powders is that there is negligible tendency for the occurrence of particle growth by either Ostwald ripening or by precipitation. This is because neither the precursor nor the desired product, are soluble in the solvent. For example, neither $BaCeO_3$ nor CeO_2 is soluble in water; only the leachable $Ba(OH)_2$ is soluble in water. Since the product is nanosize, it could be argued that its solubility may be higher than bulk materials. It is known, for example, that the solubility of a sparingly soluble species is related to its size by the following equation;

$$C(r) \approx C(\infty) \exp \left[\frac{2\gamma\Omega}{rk_B T} \right]$$

where, $C(\infty)$ is the bulk solubility (particle of a large radius), $C(r)$ is the solubility of a particle of radius r , γ is the particle-solvent interfacial energy, Ω is the molecular volume of the particle, k_B is the Boltzmann constant, and T is the absolute temperature. Assuming the following values for the various parameters; particle radius, $r \sim 2$ nm, interfacial energy, $\gamma \sim 0.5$ J/m², molecular volume, $\Omega \sim 0.125$ nm³ (125 Å³), and the temperature, $T = 350^\circ$ K, then the ratio $C(r)/C(\infty)$ is about 3.6. This shows that as long as $C(\infty)$ is rather low, even for nanosize particles the solubility enhancement is not large enough to cause any Ostwald ripening. Thus, there should be negligible particle growth.

Sintering Behavior of Powders

The sintering (densification) behavior of nanosize powders synthesized by the present invention is expected to result in densification at lower temperatures, resulting in a finer microstructure.

Characterization of Sintered Bodies

The grain size of sintered bodies made from the nanosize powders should be smaller than those made from conventional ceramic powders. It is well known that very fine-grained ceramics often exhibit interesting properties, such as, for example, superplasticity at elevated temperatures, and high strength at low temperatures.

Metallic Powders

The present invention is also applicable to the synthesis of metallic powders, by the appropriate choice of the metallic precursor and the selective solvent. For example, synthesis of Pd powder can be achieved with precursor of an equimolar alloy of Ba and Pd, which is actually a line compound BaPd. The alloy can be made by arc melting or by powder metallurgy. The powdered alloy is then treated in dilute HCl to remove the Ba to form nanosize Pd.

Suitability for the Synthesis of Large Quantities of Nanosize Powders

The process of the invention for the synthesis of nanosize powders is simple, and can be adapted by using chemical leaching technology. Especially with water as the solvent, the process does not require exotic equipment nor exotic precursors. The precursors can be made by simple calcination or alloy fabrication methods. The starting particle size of the precursors need not be very small. Finally, the process has a general applicability for a wide range of materials. The process thus is easily amenable to scale up for production of large quantities of materials.

In summary, nanosize powders of a variety of materials are usually made by one or more processes which may be categorized as belonging to molecular synthesis wherein particles are built up by an atom-by-atom or a molecule-by-molecule addition on a particle nucleus. The present invention is based on molecular decomposition wherein unwanted species are chemically leached away thus producing a nanosize powder as a residue, starting with a precursor of a macroscopic size. The method of the present invention should result in nanosize particles of a uniform composition and size. In the present invention, neither the precursor nor the product is soluble in the reaction medium. As a result, particle coarsening is not expected to occur.

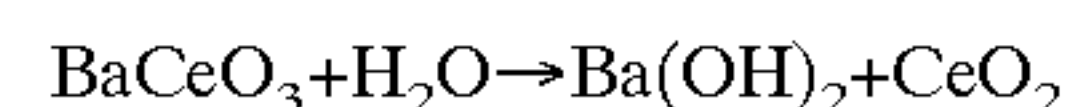
EXAMPLES

The following describes a general approach of the practice of the invention with two illustrative examples; namely the synthesis of nanosize CeO_2 and ZrO_2 .

Example I

Synthesis of Nanosize CeO_2

The starting precursor may be one of the alkaline earth cerates, such as $BaCeO_3$. At room temperature, the standard free energy for the reaction



is -189.79 kJ/mol. indicating that this reaction is favored. The volume of CeO_2 per molecule is ~ 77 Å³ and the linear dimension is (cube root of the volume) 4.25 Å. The volume per molecule of $BaCeO_3$ is ~ 85 Å³ and the linear dimension is 4.4 Å. Thus, if BaO is leached out as $Ba(OH)_2$, the change in volume for the original $BaCeO_3$ is $((85-77)/85) \times 100$ or 9.4% , or the change in linear dimension is $((4.4-4.25)/4.4) \times 100$ or 3.4% . FIG. 1 shows a schematic of a particle **11** reacting with H_2O to form $Ba(OH)_2$. The $Ba(OH)_2$ formed dissolves into water thus leaving a porous layer **13** of CeO_2 . The volume percent porosity in the layer is expected to be about 9.4% . The fact that $BaCeO_3$ readily reacts with water suggests that the porosity is open. This facilitates the transport of the reacting species, H_2O here, to the CeO_2 (porous)/ $BaCeO_3$ (dense) interface **15**. The reaction continues until all of the $BaCeO_3$ **17** reacts to form porous CeO_2 . The formed CeO_2 should be fragile and break into a fine, nanosize powder.

In order to verify the concept, the following preliminary experiments were done. Gd_2O_3 -doped $BaCeO_3$ powder of

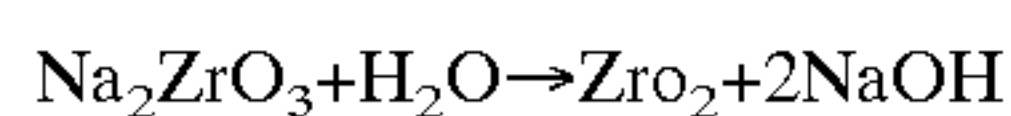
composition $\text{BaGd}_{0.2}\text{Ce}_{0.8}\text{O}_{(38)}$ was synthesized using BaCO_3 , CeO_2 , and Gd_2O_3 powders. The powders were mixed in requisite proportions and wet ball-milled for 24 hrs. The well-mixed powder was then dried and calcined at 1450°C . for 6 hrs. The calcined powder was then ball-milled and examined by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation to ensure the existence of a single-phase perovskite (FIG. 2(a)). The calcined powder was then boiled in water for 2 days, filtered using a fine filter paper, washed with water to dissolve away $\text{Ba}(\text{OH})_2$, dried and then examined by XRD. FIG. 2(b) shows the corresponding XRD trace. Also shown in FIG. 2(c) is an XRD trace of as-received CeO_2 . A comparison of FIGS. 2(a) and 2(b) shows that upon boiling, BaCeO_3 completely decomposes. The sharp peak at $\sim 24^\circ$ is due to remnant $\text{Ba}(\text{OH})_2$ not removed completely during washing.

A comparison of FIGS. 2(b) and 2(c) shows that the powder formed upon boiling is indeed CeO_2 (presumably Gd-doped). The important difference between the two is that the XRD peaks of the powder formed by boiling BaCeO_3 are considerably broader than for the as-received CeO_2 powder. Using the Scherrer formula, the particle size of the ceria formed is estimated to be ~ 4 nm. This shows that the method of the present invention involving molecular decomposition of starting a starting material with a larger molecule can lead to a fine, nanosize powder even when the initial powder is quite coarse.

Example II

Synthesis of Nanosize ZrO_2

The starting precursor may be a suitable alkali or alkaline earth zirconate. In the preliminary work, Na_2ZrO_3 was used as the precursor. This was simply boiled in water for a few minutes. The reaction is

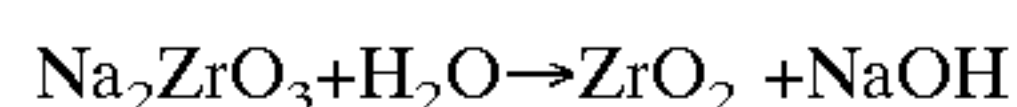


No thermodynamic data are available. However, preliminary experimental work, results of which are described below, shows that the above reaction is indeed favored.

Powder of Na_2ZrO_3 was purchased from a commercial vendor. Approximately 10 gms. of the powder was boiled in water for ten minutes. The residue was filtered, washed, and dried. The residue was subsequently examined by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. The residue was then subjected to a number of thermal treatments. The following are the results of this experiment.

FIG. 3(a) is an XRD trace of the as-received Na_2ZrO_3 powder. Sharp peaks indicate a relatively coarse (at least a few tenths of a micron or more) particle size. Very tiny peaks at approximately 28 and 31.5 degrees are due to a small amount of monoclinic ZrO_2 that was present in the as-received Na_2ZrO_3 powder.

FIG. 3(b) is an XRD trace of the residue after boiling Na_2ZrO_3 in water for 10 minutes, washing and drying. The trace shows the absence of the original Na_2ZrO_3 powder. The trace mainly consists of two very broad peaks. These peaks belong to the cubic phase of ZrO_2 . The peaks are very broad and contain more than one peak in each of the peaks. These very broad peaks are indicative of a very fine (nano) particle size. The reaction that occurred is the following:



The two sharp peaks at ~ 28 and ~ 31.5 degrees are again due to the small amount of monoclinic ZrO_2 , present in the original Na_2ZrO_3 powder.

Note that the intensity scales in 3(a) and 3(b) are quite different, and that the same monoclinic peaks with about the same intensities are present in Na_2ZrO_3 . Note also that the

integrated peak intensity of the monoclinic peak is very small compared to that of the nanosize ZrO_2 formed (broad peaks). Some growth of the original monoclinic ZrO_2 particles is expected by the deposition of new ZrO_2 (by the above reaction) on them. These monoclinic ZrO_2 particles are not expected to be nanosize, consistent with observations.

FIG. 3(c) is an XRD trace of the residue after heating in air to 100°C . for 1.5 hours. Note that the trace is similar to that in FIG. 3(b).

FIG. 3(d) is an XRD trace of the residue after 1.5 hours in air at 200°C . in air. The peaks have become somewhat sharper (peak widths are less in this figure as compared to that in FIGS. 3(b) and 3(c)). This is indicative of a slight coarsening of particles.

FIG. 3(e) is an XRD trace of the residue after 1.5 hours in air at 300°C . The peaks not only have become sharper but that the initial very broad peaks of the residue have now split into more peaks. A total of 4 broad peaks are apparent, in addition to the two sharp peaks corresponding to the original monoclinic ZrO_2 . The four broad peaks are identified with cubic ZrO_2 . The peaks correspond to (111), (200), (220), and (311) reflections, in increasing diffraction angle.

FIG. 3(f) is an XRD trace of the residue after 1.5 hours in air at 350°C . The four peaks have become slightly sharper.

FIG. 3(g) is an XRD trace of the residue after 1.5 hours in air at 400°C . The four peaks have become even sharper.

FIG. 3(h) is an XRD trace of the residue after 1.5 hours in air at 500°C .

FIG. 3(i) is an XRD trace of the residue after 1.5 hours in air at 600°C .

The corresponding XRD traces in FIGS. 3(c) to 3(i) show the formation of cubic zirconia as the residue is heated to higher temperatures. The stable phase of ZrO_2 at low temperatures is monoclinic. The formation of a very fine (nanosize) ZrO_2 by the described process leads to the stabilization of cubic ZrO_2 due to surface energy considerations ($\gamma_{\text{Cubic}} < \gamma_{\text{Monoclinic}}$ where γ denotes surface energy of the respective polymorph). The present experiment showed that: (1) Na_2ZrO_3 can be used to synthesize nanosize ZrO_2 . (2) The nanosize ZrO_2 formed is of cubic crystal structure. Using the Scherrer formula, which relates the particle size, d , to peak broadening, B , diffraction angle, θ , and X-ray wavelength, λ , by

$$d = \frac{0.9\lambda}{B \cos \theta}$$

the particle size of the ZrO_2 formed as a function of subsequent heat treatment temperature was calculated. The calculated particle size as a function of thermal treatment is given in Table A.

TABLE A

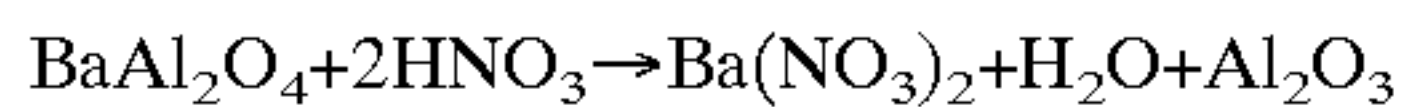
Nanosize ZrO_2 powders produced by reaction of Na_2ZrO_3 with water.

Temperature ($^\circ\text{C}$.)	Corrected (111) Peak Width (rad)	Particle Size (nm)
300	0.0476	3.4
350	0.0371	4.3
400	0.0164	9.8
500	0.0124	13.0
600	0.0113	14.2

The preceding two examples demonstrate the approach and the potential of the present invention for the synthesis of nanosize oxide powders.

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The preceding shows that nanosize CeO_2 and ZrO_2 can be produced respectively by leaching out BaO from BaCeO_3 , as Ba(OH)_2 and Na_2O from Na_2ZrO_3 , as NaOH . Various other reacting species can also in principle be used. As an example, let us examine the formation of Al_2O_3 starting with BaAl_2O_4 by reacting it with HNO_3 by the following reaction.



The free energy for the above reaction at room temperature is -255.35 kJ/mol. The change in volume upon removing BaO is $\sim 59\%$ and the change in linear dimension is $\sim 17\%$. Note that volume percent porosity in this case is much higher than for $\text{BaCeO}_3 \rightarrow \text{CeO}_2$ conversion and the reaction is expected to progress with ease. In general, the greater the amount of material that has to be leached away per unit amount of the desired final product, the finer should be the particle size. In this context, with $\text{Ba}_3\text{Al}_2\text{O}_6$ as a precursor is superior since three molecules of BaO have to be removed to form one molecule of Al_2O_3 . The standard free energy for the reaction.

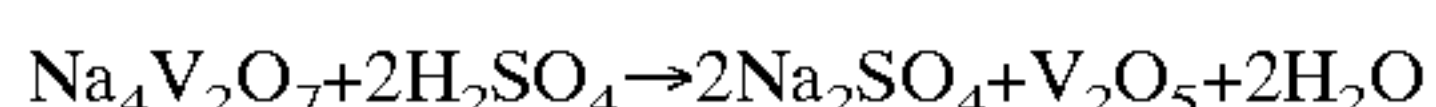


at room temperature is -884.15 kJ/mol. indicating that the reaction is favored. The percent change in volume per one molecule of Al_2O_3 formed is greater than with BaAl_2O_4 , implying a greater porosity, potentially faster kinetics, and a potentially finer particle size. A similar reaction can be envisioned with H_2CO_3 as the reactant. However, BaCO_3 has negligible solubility in water. With HNO_3 as the reactant, several reactions are possible. One such successfully conducted in our laboratory is the reaction of MgTiO_3 with HNO_3 to form $\text{Mg(NO}_3)_2$ and TiO_2 given by



The above reaction is thermodynamically favored at room temperature. Also, $\text{Mg(NO}_3)_2$ is water soluble. Preliminary experiments were done wherein MgTiO_3 was boiled in dilute HNO_3 for 11 hours. The reaction went to completion and the resulting TiO_2 was indeed nanosize, as judged by XRD peak broadening. The XRD traces are not given here for the sake of brevity.

The preceding discussion was on reactions of precursor powders with HNO_3 . It is also possible and advantageous to use H_2SO_4 since the magnitudes of standard free energies ($|\Delta G^\circ|$ with $\Delta G^\circ < 0$) of the corresponding reactions are often larger with H_2SO_4 than with HNO_3 . As an example of the use of SO_3 , consider the synthesis of V_2O_5 , which is used as a catalyst in NO_x reduction, starting with $\text{Na}_4\text{V}_2\text{O}_7$. Reaction with SO_3 is given by



with the standard free energy at room temperature given by -326.4 kJ/mol.

Also, Na_2SO_4 is highly soluble in many polar liquids including of course water. Also, as long as $\text{Na}_4\text{V}_2\text{O}_7$ is present, VOSO_4 will not form.

In the preceding paragraphs, several reactions in water as a solvent are described. In some cases, the use of water as a solvent may lead to the formation of hydroxides, e.g. Al(OH)_3 . In such cases, instead of acids, the suitable reactants may be the respective gases; e.g. N_2O_5 instead of HNO_3 and SO_3 instead of H_2SO_4 , and non-aqueous, polar solvents. The advantage of using non-aqueous solvents is that there is no possibility of the formation of Al(OH)_3 ,

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which must be heated to remove water thus risking agglomeration and coarsening. The possible use of other solvents is discussed below. Table B gives a few of the possible reactions to form a number of oxide powders. All of the reactions are given with reactive gaseous species. Similar data can readily be given with aqueous acids as well.

TABLE B

Some examples of the synthesis of fine ceramic powders by the present invention.

Ceramic Of Interest	Precursor	Chemical Reaction with Selective Solvent	Standard Free Energy, ΔG° (kJ/mol.)
Al_2O_3	BaAl_2O_4	$\text{BaAl}_2\text{O}_4 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{Al}_2\text{O}_3$	-113.19
Al_2O_3	$\text{Ba}_3\text{Al}_2\text{O}_6$	$\text{Ba}_3\text{Al}_2\text{O}_6 + 3\text{CO}_2 \rightarrow 3\text{BaCO}_3 + \text{Al}_2\text{O}_3$	-459.51
Al_2O_3	NaAlO_2^*	$2\text{NaAlO}_2 + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3$	-342.6
Cr_2O_3	MgCr_2O_4	$\text{MgCr}_2\text{O}_4 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{Cr}_2\text{O}_3$	-6.93
Cr_2O_3	MgCr_2O_4	$\text{MgCr}_2\text{O}_4 + \text{SO}_3 \rightarrow \text{MgSO}_4 + \text{Cr}_2\text{O}_3$	-188.13
ZrO_2	BaZrO_3	$\text{BaZrO}_3 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{ZrO}_2$	-88.33
ZrO_2	BaZrO_3	$\text{BaZrO}_3 + \text{SO}_3 \rightarrow \text{BaSO}_4 + \text{ZrO}_2$	-336.14
ZrO_2	BaZrO_3	$\text{BaZrO}_3 + \text{N}_2\text{O}_5 \rightarrow \text{Ba(NO}_3)_2 + \text{ZrO}_2$	-260.3
TiO_2	MgTiO_3	$\text{MgTiO}_3 + 2\text{HNO}_3 \rightarrow \text{Mg(NO}_3)_2 + \text{TiO}_2 + \text{H}_2\text{O}$	-81.07
TiO_2	Mg_2TiO_4	$\text{Mg}_2\text{TiO}_4 + 2\text{CO}_2 \rightarrow 2\text{MgCO}_3 + \text{TiO}_2$	-77.34
TiO_2	Mg_2TiO_4	$\text{Mg}_2\text{TiO}_4 + 2\text{SO}_3 \rightarrow 2\text{MgSO}_4 + \text{TiO}_2$	-440.82
TiO_2	Na_2TiO_3	$\text{Na}_2\text{TiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{TiO}_2$	-80.62
TiO_2	Na_2TiO_3	$\text{Na}_2\text{TiO}_3 + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{TiO}_2$	-325.81
V_2O_5	$\text{Na}_4\text{V}_2\text{O}_7$	$\text{Na}_4\text{V}_2\text{O}_7 + \text{SO}_3 \rightarrow 2\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$	-458.01

*Standard free energy for $3\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \rightarrow 3\text{Na}_2\text{O} + \text{Al}_2(\text{SO}_4)_3$ at 298 K is $+1,155$ kJ/mol. showing that the formation of Na_2SO_4 is favored over that of $\text{Al}_2(\text{SO}_4)_3$. Thus, reaction of NaAlO_2 with SO_3 should proceed as shown. Also, while this reaction can be effected in water, a preferred is to identify a solvent with a high solubility for Na_2SO_4 but negligible for NaAlO_2 . This is because of the possible formation of alumina precipitate which would tend to grow the particles. The formation of alumina using an aqueous solution of NaAlO_2 would be the conventional chemical precipitation process, and it is anticipated that in such a case a careful control of parameters would be necessary to prevent particle growth.

Table B shows that the standard free energies of the reactions are all negative suggesting that all of these reactions are thermodynamically favored. Carbonates, sulfates or nitrates of Al, Ti, and Zr are less stable than the corresponding alkaline earth compounds. No thermodynamic data appear to be available for the former.

Non-aqueous Solvents

Reactions of the various oxides with CO_2 , N_2O_5 , and SO_3 to respectively form carbonates, nitrates, and sulfates can in principle be carried out in water or other polar liquids. $\text{Ba(NO}_3)_2$ is soluble in water, but BaCO_3 and BaSO_4 are essentially insoluble. There are a number of nonaqueous, polar liquids as possible candidates. The prospective solvent to be used must have the following characteristics: (1) It must have a reasonable solubility for the reacting gases, namely, CO_2 , SO_3 or N_2O_5 . (2) It must have a significant solubility for BaCO_3 , BaSO_4 or $\text{Ba(NO}_3)_2$. Table C gives a list of possible candidates and their physical properties. It is important to note that the boiling points of these liquids are quite high. Thus, as long as the solvent does not chemically react with either the precursor or the product, the process can be carried out over a wide temperature range. Also, the solubilities of BaCO_3 , BaSO_4 and $\text{Ba(NO}_3)_2$ should be greater at higher temperatures. At the same time, however, the solubilities of the reacting gases in liquids decreases with an increasing temperature. Thus, a suitable optimum temperature must be identified at which the reaction rate is maximum.

TABLE C

Physical properties of some nonaqueous, polar liquids.						
Material	Formula	b.p. (° C.)	m.p. (° C.)	Viscosity (millipois)	Dielectric Constant	Density (g/ml)
Formamide	HCONH ₂	210.7	2.55	39.7 at 20° C.	111.5 at 20° C.	1.135 at 18° C.
N-Methyl-acetamide	CH ₃ CONHCH ₃			24.13 at 50° C.	151.8 at 50° C.	0.9336 at 50° C.
N-Methyl-formamide	HCONHCH ₃	180	-5.4	19.9 at 15° C.	200.1 at 15° C.	1.007 at 15° C.
N-Methyl-propionamide	C ₂ H ₅ CONHCH ₃			60.6 at 20° C.	185 at 20° C.	0.9347
Propylene Carbonate		241	-49	25.3	64.4	1.19
Ethylene Carbonate	(CH ₂ O) ₂ CO	248	39	18.5	89.6 at 40° C.	1.3218 at 39° C.

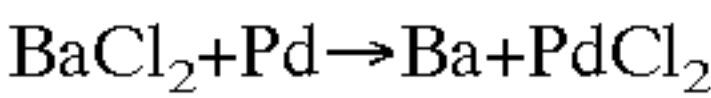
The method of the present invention can also be used to synthesize doped powders. For example, if the desired powder is Y₂O₃-doped ZrO₂ of composition Zr_(1-x)Y_xO_(2-δ), then the starting precursor could be BaZr_(1-x)Y_xO_(3λ). After reaction with HNO₃, as an example, the resulting powder should be Zr_(1-x)Y_xO_(2δ). Another example is RE-doped CeO₂, where RE is a rare earth, namely Ce_(1-x)RE_xO_(2δ), which can be made using doped BaCeO₃, that is, BaCe_(1-x)RE_xO_(3λ). In the preliminary work, nanosize Gd-doped CeO₂ was synthesized.

As already discussed, the method of the present invention can be used with water as the solvent in many cases. With water as the solvent, the corresponding aqueous acids, namely H₂CO₃ or H₂SO₄ or HNO₃, can be used, the choice of the acid being dependent upon the solubility of the leachable compound to be formed, assuming of course that the thermodynamics are favorable. For example, the synthesis of nanosize TiO₂ starting with MgTiO₃ using HNO₃ has been demonstrated. Further, if the leachable compound is Na₂SO₄ as in the formation of V₂O₅ starting with Na₄V₂O₇, H₂SO₄ should be the acid. However, with barium-containing compounds, HNO₃ is the acid of choice. There are two potential problems with water, however. (i) There is the potential for hydroxide formation. (ii) Agglomeration has been shown to occur readily when water is present. This may be avoided by replacing water with another solvent, and/or by supercritical drying. For the synthesis of RE-doped CeO₂ starting with BaCe_(1-x)RE_xO_(3λ) as a precursor, water is the ideal solvent since cerium hydroxide does not readily form. Preliminary work, discussed earlier, has indeed shown that nanosize ceria can be formed in an aqueous medium.

Example III

Synthesis of Nanosize Metallic Powders

The present invention should also be useful for the synthesis of nanosize metallic powders, provided suitable intermetallic compounds can be used as precursors. There are numerous binary and ternary intermetallic compounds which may be used as precursors. As an example, for the synthesis of nanosize Pd, a possible precursor is BaPd which is an intermetallic line compound. The possible approach would consist of first fabricating BaPd by a conventional metallurgical process and then reacting it with an acid, e.g., HCl acid. It is readily shown that the ΔG° for the reaction,



is positive suggesting that the first compound to form will be BaCl₂. The BaCl₂ formed will dissolve into water thus

forming nanosize Pd powder. The so-formed Pd powder should be nanosize and continue to remain nanosize since Pd has a negligible solubility in water. Thus, as long as the concentration of HCl is low, and there is BaPd to react with, that is, there is Ba to react with HCl; PdCl₂ will not form. Note that this process differs from the synthesis of Pd by the reduction of PdCl₂. In the latter case, particle growth of Pd readily occurs since the deposition of Pd on the already formed Pd powder continues to occur as PdCl₂ in solution reacts with a reducing agent, e.g., an alkali metal borohydride. In such a case, the experimental conditions must be carefully controlled to prevent particle growth. By contrast, the process of the present invention should readily lead to the formation of nanosize Pd with negligible particle growth.

Advantages of the Method of the Present Invention over the other Synthesis Methods for Nanosize Powders

1) Uniform Mixing at a Molecular or an Atomic Level

Since the powders are produced by leaching unwanted constituents from an initial homogeneous solid solution or a compound, the remaining constituents should be intimately mixed. For example, in the synthesis of Gd₂O₃-doped CeO₂ starting with BaCe_(1-x)Gd_xO_(3δ), Gd and Ce are expected to be intimately mixed since the original solid solution is uniform.

2) Narrow Particle Size Distribution

Since the constituent to be removed, e.g., Ba is distributed on a regular, periodic basis, it is anticipated that molecular level cracks or fissures are formed when Ba is removed as Ba(OH)₂ or Ba(NO₃)₂. This should lead to a uniform particle size.

3) Negligible Growth of Nanosize Particles Unlike in Conventional Chemical Synthesis

The resulting nanosize particles in the present invention are essentially insoluble in the liquid media used, and so are the precursors. As a result, growth is not expected unlike conventional chemical synthesis approaches which rely on precursors reacting in solution to form an insoluble product; e.g., the formation of insoluble Fe₃O₄ from Fe(II) and Fe(III) chlorides in solution. In such cases, growth of particles can readily occur.

While this invention has been described with reference to certain specific embodiments and examples, it will be recognized by those skilled in the art that many variations are possible without departing from the scope and spirit of this invention, and that the invention, as described by the claims, is intended to cover all changes and modifications of the invention which do not depart from the spirit of the invention.

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What is claimed is:

1. A process for forming a nanosize ceramic powder comprising:

forming a precursor ceramic material comprising a fugitive constituent and a non-soluble constituent in a single phase;

decomposing the fugitive constituent to leave the non-soluble constituent by contacting the precursor ceramic material with a selective solvent to form a solution of the fugitive constituent in the solvent and a non-dissolved residue of the non-soluble constituent,

the precursor ceramic material being sufficiently reactive with the solvent to form the solution of the fugitive constituent in the solvent and form the non-dissolved residue of the non-soluble constituent,

the precursor ceramic material and the non-dissolved residue being sufficiently insoluble in the solvent such that there is essentially no precursor ceramic material and non-dissolved residue in the solution that will deposit and precipitate upon the residue of the non-soluble-constituent,

the fugitive constituent being sufficiently soluble in the solvent such that the decomposing is without deposition or precipitation of dissolved fugitive constituent upon the residue of the non-soluble constituent,

removing the solution of the fugitive constituent from the residue to form a nanosize powder of the residue of the non-soluble constituent.

2. The process as in claim 1 wherein the precursor ceramic material is $\text{BaCe}_{(1-x)}\text{RE}_x\text{O}_{3-\delta}$ or $\text{SrCe}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ and the composition of the nanosize powder is $\text{Ce}_{1-x}\text{RE}_x\text{O}_{2-\delta}$ where RE is a rare earth metal or Y, x is between 0 and about 0.25, and δ is between 0 and about 0.13.

3. The process as in claim 1 wherein the precursor ceramic material is $\text{SrZr}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ or $\text{BaZr}_{1-x}\text{RE}_x\text{O}_{3-\delta}$ and the composition of the nanosize powder is $\text{Zr}_{1-x}\text{RE}_x\text{O}_{2-\delta}$ where RE is a rare earth metal or Y, x is between 0 and about 0.25, and δ is between 0 and about 0.13.

4. The process as in claim 1 wherein the composition of the nanosize powder is Al_2O_3 .

5. The process as in claim 3 wherein the precursor ceramic material is selected from the group consisting of BaAl_2O_4 , $\text{Ba}_3\text{Al}_2\text{O}_6$, and NaAlO_2 .

6. The process as in claim 1 wherein the composition of the nanosize powder is Cr_2O_3 .

7. The process as in claim 6 wherein herein the precursor ceramic material is MgCr_2O_4 .

8. The process as in claim 1 wherein the composition of the nanosize powder is ZrO_2 .

9. The process as in claim 8 wherein the precursor ceramic material is BaZrO_3 .

10. The process as in claim 1 wherein the composition of the nanosize powder is TiO_2 .

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11. The process as in claim 10 wherein the precursor ceramic material is MgTiO_3 , or Mg_2TiO_4 .

12. The process as in claim 1 wherein the composition of the non-soluble constituent and the nanosize powder is V_2O_5 .

13. The process as in claim 12 wherein the precursor ceramic material is $\text{Na}_4\text{V}_2\text{O}_7$.

14. The process as in claim 1 wherein the selective solvent is water.

15. A process for forming a nanosize ceramic powder comprising:

forming a precursor ceramic material comprising a fugitive constituent and a non-soluble constituent in a single phase;

decomposing the fugitive constituent to leave the non-soluble constituent by contacting the precursor ceramic material with a selective solvent to form a solution of the fugitive constituent in the solvent and a non-dissolved residue of the non-soluble constituent,

the precursor ceramic material being sufficiently reactive with the solvent to form the solution of the fugitive constituent in the solvent and form the non-dissolved residue of the non-soluble constituent,

the precursor ceramic material and the non-dissolved residue being sufficiently insoluble in the solvent such that there is essentially no precursor ceramic material and non-dissolved residue in the solution that will deposit and precipitate upon the residue of the non-soluble-constituent,

the fugitive constituent being sufficiently soluble in the solvent such that the decomposing is without deposition or precipitation of dissolved fugitive constituent upon the residue of the non-soluble constituent,

removing the solution of the fugitive constituent from the residue to form a nanosize powder of the residue of the non-soluble constituent, where the selective solvent is an acid.

16. The process as in claim 15 wherein the acid is selected from the group consisting of HNO_3 , HCl , H_2CO_3 and H_2SO_4 .

17. The process as in claim 15 wherein the acid contacted with the precursor ceramic material is an acid gas.

18. The process as in claim 17 wherein the acid gas is SO_3 , N_2O_5 , CO_2 or HCl .

19. The process as in claim 1 wherein the selective solvent is a reacting gas dissolved in a non-aqueous polar solvent.

20. The process as in claim 19 wherein the polar solvent is selected from the group consisting of formamide, N-methyl-acetamide, N-Methyl-formamide, N-Methyl-propionamide, propylene carbonate, and ethylene carbonate, and the reacting gas is selected from the group consisting of CO_2 , SO_3 , SO_2 and N_2O_5 .

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,803,027 B1
DATED : October 12, 2004
INVENTOR(S) : Virkar et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,

Item [22], Filed, replace "Oct. 26, 1998" with -- Oct. 26, 1999. --

Signed and Sealed this

First Day of February, 2005

A handwritten signature in black ink, reading "Jon W. Dudas", is written over a rectangular area with a light gray dotted background.

JON W. DUDAS

Director of the United States Patent and Trademark Office